Using Cyanex 923 for selective extraction in a high concentration chloride medium on nickel metal hydride battery waste

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ABSTRACT

The extraction properties of the solvating extractant trialkylphosphine oxide mixture Cyanex 923 have been investigated using liquid–liquid extraction methods on leach liquors from nickel metal hydride batteries dissolved in 8 M hydrochloric acid. Separation routes for leach liquors from individual electrode materials and a mixed material were developed. The batteries used in this study contained thirteen metals and the developed separation schemes separate them in up to four fractions. The main fraction in each case contains nickel, also potassium and magnesium if present in the feed. Part of the nickel raffinate is refluxed to the dissolution step in order to reduce the amount of metals to be extracted into the organic phase. A nitrate strip step separates the cobalt and manganese from the lanthanoid content, since lanthanoid nitrate complexes are extracted.

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1. Introduction

The recovery of metals from used batteries should be a natural part of attaining sustainable society. In the case of nickel metal hydride batteries (NiMH) they are and have been used for an extended time in a number of applications e.g. hybrid electric vehicles. There are large amounts of these batteries being recycled and requiring recycling in the near future. Therefore, developing and improving processes for the treatment of NiMH batteries is of high importance.

Several methods using liquid–liquid extraction for metal recovery from nickel metal hydride battery recycling have been suggested in literature (Li et al., 2009; Rodrigues and Mansur, 2010; Tzanetakis and Scott, 2004; Zhang et al., 1998, 1999). Primarily the different methods use 1-3M hydrochloric or sulphuric acid to create leach liquors and treat them with different acidic extractants such as Cyanex 272 or D2EHPA to make the separations. The current study differs from the ones in the literature both in that a solvating extractant (Cyanex 923) and more concentrated leach solutions (8 M chloride) are used to reduce volumes and improve metal recovery.

In hydrometallurgical treatment, minimization of the volume and reducing the complexity of the aqueous flows that require treatment can give easier separations and more sustainable and cost effective processes. This means that treatment facilities can also be made smaller, requiring less energy and chemicals. In this work the volume is minimized by using concentrated systems and selective leaching.

The complexity of the aqueous flows is reduced by using individual electrode materials and by removing groups of elements by the use of solvating extractants.

Certain solvating extractants are capable of extracting groups of metals with similar chemical properties. This extraction can be achieved without requiring a modification of solution parameters by the addition of chemicals, such as raising the pH for extraction as acidic extractants often require. Removing the need for chemical addition during extraction also reduces the need for parameter monitoring in a process and thereby makes a process simpler and more robust. This makes solvating extractants with relevant extraction properties suitable for a pre-step treatment of the battery waste streams. Such pre-treatment can potentially be able to harmonize the anode and cathode streams, i.e. remove the elements that differ between the streams. This could allow for the combination of the treatment of, for example, nickel from initially separated cathode and anode streams. Cyanex 923 is a solvating extract with suitable properties for extracting chloride complexes and was chosen for this study.

Previous work in the form of a general study into the properties of hybrid electric vehicle (HEV) nickel metal hydride batteries showed a large difference in composition for the electrode materials (Larsson et al., in press). This opened up for the possibility of developing separate recycling processes for the anode and cathode electrode materials. This separation has the benefit of reducing the number of metals from the combined 13 metals to 9 for the cathode and 11 for the anode. Since a mixed fraction is close to unavoidable on an industrial scale a mixed fraction was investigated along with the cathode and

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anode fractions. The study also showed that hydrochloric acid is a suitable medium from a dissolution standpoint, since it can avoid dissolving nickel metal.

The benefit of high concentrations is the reduction in flow volume. However, this can easily lead to loading of the organic solvent if the majority species is to be extracted. In nickel metal hydride batteries the dominating species is nickel which extracts poorly in chloride media for solvating extractants due to the fact that nickel does not form easily extractable chloride complexes and therefore remains in the aqueous phase. The benefit that is drawn from this is that only the minor constituents of the battery are extracted and the loading of the organic phase is limited and concentrated systems are thereby possible. With proper organic to aqueous ratios in the extraction and strip steps, the concentration of the less abundant metals can be raised. A potential problem with concentrated system is precipitation, chloride salts of the relevant elements are, however, soluble even at high concentrations (Haynes, 2011).

The objective of this study was to find suitable conditions for the extraction systems and the initial solutions to allow for selective extraction of metals from the leach solutions, preferably attaining a purified aqueous stream of nickel. Parameters which affect the extraction include the extractant concentration, aqueous counter-ion concentrations (and equivalent metal concentration), acidity (and its related counter-ion contribution) and phase ratios.

2. Background

The general use of Cyanex 923 has been described in a review article on organophosphorus extractants by Flett (2005). Cyanex 923 in chloride systems has previously been shown to selectively extract cadmium from nickel and cobalt in the recycling of nickel cadmium batteries (Reddy and Priya, 2006). Studies by Gupta et al. investigate the use of Cyanex 923 in high concentration chloride systems for spent catalyst and sea nodule metal recovery (Gupta et al., 2002, 2003).

Many of the published studies on Cyanex 923 are investigations where trace metal concentrations are used with acidity comparable to the counter-ion concentration, i.e. the concentration of chloride has been varied using concentrated hydrochloric acid. This differs from the aqueous phases used in this study, which are leaching liquors with a very low acidity compared to the counter-ion concentration and the metal concentration is high. This can influence the distribution ratios and a high metal concentration reduces the necessary volume.

The nickel metal hydride batteries used as raw material in this study were prismatic batteries constructed by alternate stacking of cathode and anode electrode plates. Nickel hydroxide is the main active material in the cathode electrode and is pasted onto a nickel metal mesh. The nickel hydroxide paste has additions of cobalt, zinc, yttrium, magnesium and manganese. The anode electrode plate consists of a perforated nickel-plated steel sheet onto which a hydrogen absorbing alloy has been pasted. The alloy is a nickel and mischmetal (a mixture of lanthanum, cerium, neodymium and praseodymium) alloy with substitutions of the nickel with cobalt, aluminium and manganese, there is also an addition of yttrium. For this study the electrode materials were separated by hand. However, the individual electrode materials in nickel metal hydride batteries can be separated by mechanical processes (Ito et al., 2009; Tsunekawa et al., 2007).

2.1. Cyanex 923 extraction mechanism

Cyanex 923 is a mixture of four trialkylphosphine oxides R_3PO (trioctylphosphine oxide), $R'R_2PO$ (dioctylmonohexylphosphine oxide), R'_2RPO (dihexylmonooctylphosphine oxide), R'_3PO (trihexylphosphine oxide) where R is n-octyl and R' is n-hexyland has an average molecular

weight of 348 g per mol Dziwinski and Szymanowski (1998). The trialkylphosphine oxides in Cyanex 923 are adduct formers and the general form of the extraction of metal complex adducts can in this case be written as follows:

$$M_{(aq)}^{z+} + zA_{(aq)}^- + bB_{(org)} \rightleftharpoons MA_zB_{b(org)} \qquad (1)$$
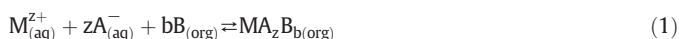
Where A is the chloride-ion, B is the adduct-forming molecule of Cyanex 923 and M is the metal ion. In acidic solutions negative chloride complexes can be extracted by the inclusion of a hydrogen ion. This has been observed as a likely extraction mechanism for zinc and iron (Dessouky et al., 2008).

$$M_{(aq)}^{z+} + yH_{(aq)}^+ + (z+y)A_{(aq)}^- + bB_{(org)} \rightleftharpoons H_yMA_{z+y}B_{b(org)} \qquad (2)$$
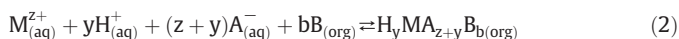
The involvement of two extractant molecules per extracted complex has been observed for nickel, cobalt and iron in chloride solutions (Gupta et al., 2003; Saji et al., 1998). Lanthanoids and yttrium with three and four extractant molecules per extracted complex have been observed in thiocyanate solutions (Reddy et al., 1998).

3. Experimental

The three types of solutions used as water-phases were made by dissolving anode material, cathode material and a mixed material. The mixed material was made by shredding whole cells and subsequently removing the whole separators and anode backing material (nickel-plated steel), which remained intact during the shredding. The used battery materials were from Panasonic prismatic module 6.5 Ah NiMH plastic casing batteries used in a hybrid electric vehicle. The solid materials were dissolved using 8 M hydrochloric acid (Acros, reagent grade). All dilutions were prepared using pure water (MilliQ, Millipore, >18 MΩ/cm). For the organic phases Cyanex 923 (95%, Cytec), tributyl phosphate (97%, Aldrich) and aliphatic kerosene distilled at 190–250 °C (Solvent 70, Statoil) were used.

The dissolution of the electrode materials was performed by keeping a constant potential in the solutions, after adding a small initial volume, by the addition of 8 M hydrochloric acid while dissolving the cathode and anode materials respectively. At the end of dissolution (when the potential remained constant without addition of acid) a small additional sample was added to the solution after separating it from the nickel metal allowing the pH of the solution to rise until no more material could be dissolved, this ensured a low acidity of the end solution. This means that the metal concentration and the chloride concentration are linked in this work as no additional chloride ions were added in the making of the leach liquors. The active cathode material is fully dissolved, the anode material leaves a small residue due to the high concentration in the leach liquor. The residue was fully dissolved in a second cycle with 8 M acid, the resulting solution added to the initial dissolution. Utilizing non-oxidizing conditions (nitrogen atmosphere) for the cathode and mixed material dissolutions has the benefit that the nickel metal in the electrode remains undissolved, reducing the cathode related acid consumption, and thereby stream volume by 37%, for further information on dissolution see Larsson et al. (in press).

The extractant concentration to investigate was determined through a series of optimization tests to be 70% (v/v) of Cyanex 923, since lower concentrations had insufficient distribution ratios for yttrium, manganese and cobalt (in batch experiments). Higher concentrations of extractant also had unsuitably high viscosity when loaded and slow phase disengagement.

The investigated chloride concentration (with its associated metal concentration) was 8 M since higher concentrations approach the solubility limits of the metal's chloride salts in the solutions and

precipitations would result at higher concentrations. The distribution ratios were also of a suitable value at 8 M chloride concentration.

The concentration of the different elements in the aqueous phases is of great importance as this will influence the extraction behavior under the influence of loading. The molar concentrations of the 8 M hydrochloric acid dissolutions are shown in Table 1. Small amounts of aluminium and iron were present in the cathode stream and will be assumed to be likely in a large-scale process and are thereby included in the process-scheme. The loading characteristics of the system are especially important in the anode and mixed systems since the non-nickel content is higher than in the cathode system (85% for the cathode versus 64% for the anode). Thereby a larger amount of metals will need to be extracted in order to leave only nickel in the aqueous phase, which can lead to loading of the organic phase. A high extractant concentration was used and phase ratios were varied in order to find suitable conditions to decrease the loading effects in the systems.

While investigating extractant and chloride concentration there was third-phase formation in some of the Cyanex 923 samples, TBP was added to the solvent to act as a phase modifier. At concentrations above 5% TBP all third phase problems were solved, the solvents were prepared using 10% TBP. It is also possible to use e.g. 1-decanol; this was tested and found equally effective.

3.1. Metal ion concentration analysis

A Thermo iCAP 6500 inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine metal concentrations in the samples. All samples were diluted using 1 M suprapur nitric acid (diluted from concentrated suprapur 65% nitric acid, Merck). Measurement uncertainties were estimated using triple samples.

3.2. Solvent extraction procedure

The extraction for different systems is represented using the distribution ratios $D = [M]_{org}/[M]_{aq}$ at equilibrium, where M is the metal of interest. The distribution ratios were determined by measuring solely the aqueous phase because of insufficient stripping of the organic phases in a one-step procedure. Concentration in the organic phase was determined by mass balance. This is reasonably accurate as the level of sorption is expected to be relatively small due to the relatively low pH and the elements involved but can limit the range of measureable distribution ratios. The aqueous (leach liquors) and organic solutions were contacted for 30 minutes (sufficient to reach equilibrium) at 25 °C in a thermostatted mechanical shaker and subsequently centrifuged. Due to the phase volume changes the potassium content was used as an internal standard to compensate

Table 1
The molar concentration of the three main aqueous solutions obtained by dissolving the materials in 8 M hydrochloric acid. The uncertainty is one standard deviation of a triple sample.

	Cathode	Anode	Mixed
Al	0.011 ± 0.0001	0.18 ± 0.004	0.09 ± 0.0017
Ce	nd	0.14 ± 0.001	0.06 ± 0.0005
Co	0.35 ± 0.03	0.22 ± 0.002	0.26 ± 0.0014
Fe	0.006 ± 0.0002	0.011 ± 0.0001	0.04 ± 0.0009
K	0.07 ± 0.001	0.006 ± 0.0001	0.07 ± 0.0022
La	nd	0.45 ± 0.005	0.19 ± 0.0054
Mg	0.082 ± 0.001	nd	0.04 ± 0.0010
Mn	0.034 ± 0.001	0.32 ± 0.004	0.15 ± 0.0031
Nd	nd	0.051 ± 0.0005	0.02 ± 0.0004
Ni	3.3 ± 0.2	2.51 ± 0.031	2.51 ± 0.075
Pr	nd	0.019 ± 0.0002	0.01 ± 0.0002
Y	0.041 ± 0.002	0.030 ± 0.0003	0.03 ± 0.0006
Zn	0.031 ± 0.001	nd	0.02 ± 0.0005
Sum	3.9	3.9	3.5
Sum - Ni, K, Mg	0.47	1.4	0.87

for this change since the potassium has a very low extraction in these systems. The post extraction organic concentration with no phase volume change:

$$C_O^{post} = \frac{V_A^{pre} \cdot C_A^{pre} - V_A^{post} \cdot C_A^{post}}{V_O^{post}} \tag{3}$$

Under the assumption that the loss of aqueous volume is the gained organic volume and that the factor k represents the loss of aqueous phase:

$$C_O^{post} = \frac{V_A^{pre} \cdot C_A^{pre} - V_A^{pre} \cdot k \cdot C_A^{post}}{V_O^{pre} + \left(V_A^{pre} - V_A^{post}\right)} \tag{4}$$

With the compensated post extraction organic concentration the distribution ratio can be calculated:

$$D = \frac{C_O^{post}}{C_A^{post}} = \frac{C_A^{pre} - k \cdot C_A^{post}}{(\theta + (1-k)) \cdot C_A^{post}} \tag{5}$$

Where θ is the organic to aqueous volume ratio. For stripping the organic concentration after the first extraction is calculated using the previous formulas and the distribution for the stripping as follows:

$$D = \frac{C_O^{pre} \cdot V_O^{pre} - C_A^{post} \cdot V_A^{post}}{V_O^{post} \cdot C_A^{post}} \tag{6}$$

Assuming constant phase volume ratio during stripping:

$$D = \frac{C_O^{pre} - C_A^{post} \cdot \frac{1}{\theta}}{C_A^{post}} \tag{7}$$

The organic phase from the single step trials did not extract sufficiently to represent an organic phase in process-like conditions. In order to investigate the stripping of the organic phase of the main extractions, in a number of nitrate and chloride media, loaded organic phases for each case were made using a 4 step counter-current process with a 2:1 O:A ratio. To determine the concentration in these organic phases the amount of stripped cobalt was used as an internal standard and compared with the original aqueous phase concentrations assuming quantitative extraction. The concentration of nickel, magnesium and potassium in the organic phase was determined using the strip phase with the highest concentration. The phase ratios of the strip experiments were not optimized and a 1:1 volume ratio was used to show possible separations with different media.

The wide range of concentrations for different metals limited the certainty of the detection methods for distribution ratios to lie mainly within 0.1–100. Distribution ratios more than one standard deviation above 100 were represented as being above 100 due to their relatively high uncertainty. Distribution ratios more than one standard deviation below 0.05 were represented as less than 0.1 to indicate their low value.

4. Results and discussion

Calculating on the average amount of trialkylphosphine oxide content in Cyanex 923 the maximum loading capacity (assuming 2 molecules per extracted complex) is 0.012 mol per percent v/v Cyanex 923 in the organic phase. So for 70% Cyanex 923 solvents, the loading likely occurs at less than 0.84 M and, as seen in Table 1, the anode and mixed material metal concentrations for the non-nickel, magnesium or potassium content exceed this value. This means that the required loading capacity needs to be raised, either by reducing the concentration or by increasing the phase ratio for the mixed material and anode cases.

The distribution data shown in Figs. 1, 2 and 3 excludes zinc and iron since their distribution ratios exceeded 100. Magnesium, potassium and nickel are also excluded since their distribution ratios had a high uncertainty but were very low.

The acidity of the aqueous solutions had some influence on the distribution ratios and a significant influence on phase-separation behavior. At low acidity the phase-separation was slow while a too high acidity in turn gave the organic phase too high viscosity. The phase modifier TBP reduced these effects. The experiments using cathode based leach liquors were performed with a 0.16 M hydrogen ion addition after dissolution. The systems based on leached anode and mixed material were used without increased acidity, since a lowered pH reduced the distribution ratio especially of lanthanoids.

4.1. Extraction behavior of chloride based cathode leach solutions with Cyanex 923

The influence of the phase ratio on loading effects for the cathode chloride system was investigated using the 70% Cyanex 923, 10% TBP and 20% kerosene system; results shown in Fig. 1. Calculating from the molar concentrations in Table 1 and assuming that Cyanex 923 forms adducts in a 2:1 ratio for each complex then the 1:1 phase ratio should be sufficient to avoid loading assuming no nickel is extracted. The experimental results show clear loading effects at phase ratios below 2, since the distribution ratios increase, without a loading effect the distribution ratio would have remained approximately constant as it does for the phase ratios above 2. There is negligible advantage in increasing the phase ratio for the cathode system above 1.5 since the distribution ratio for the minor metals is not increased.

4.1.1. Stripping characteristics

The ability to strip a loaded organic phase after contacts with a cathode based leach liquor was investigated using chloride and nitrate solutions with and without acid using sodium salts and acids, the results are presented in Table 2. Cobalt, manganese and aluminium are all stripped to a high degree in all cases except in the 1 M nitrate case where aluminium remains extracted and manganese has a distribution ratio of 3.5. Yttrium is stripped using the low concentration chloride solutions but remains extracted in nitrate systems, increased acidity leads to increased stripping. This indicates that a separation of yttrium from cobalt and manganese can be made using a nitrate stripping agent, more generally this indicates that the trivalent metals can be similarly separated in this type of system. Zinc
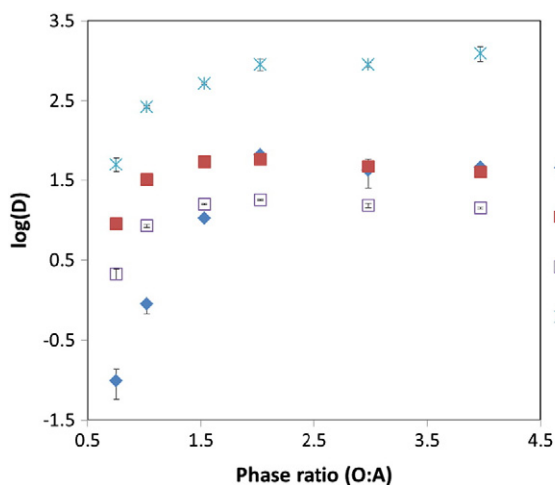

Fig. 2. Distribution ratios for 8 M chloride leach solutions based on active anode material, see Table 1 for concentrations, with a 70% Cyanex 923, 10% TBP and 20% kerosene concentration. Nickel and potassium excluded due to their low distribution ratios.

and iron are not stripped other than by 5 M nitric acid (zinc) in the tested cases. This indicates that zinc and iron should be extracted in a pre-step in order to be able to use a more suitable strip phase.

The loaded organic phases contained less than 1% of the nickel and potassium in the original aqueous phase and subsequently stripped. For magnesium approximately 2.3% was extracted from the original aqueous phase and it was stripped fully with all tested stripping agents.

4.1.2. Low extractant concentration for the removal of zinc and iron

Iron and zinc can be selectively extracted from the 8 M cathode solutions using a low extractant concentration in the organic phase. A distribution ratio exceeding 10 is achieved at 8 % (v/v) Cyanex 923 concentration with the other metal constituents having a distribution ratio below 0.2. The lower extractant concentration allows for an easier stripping of zinc and iron than from a 70% (v/v) Cyanex 923 organic phase. The extraction of metals other than zinc and iron is relatively low and a hydrochloric acid scrub step can remove any

Fig. 1. Distribution ratios for 8 M chloride leach solutions based on active cathode material, see Table 1 for concentrations, with a 70% Cyanex 923, 10% TBP and 20% kerosene concentration. Zinc and iron excluded due to their high distribution ratios. Nickel, potassium and magnesium excluded due to their low distribution ratios.
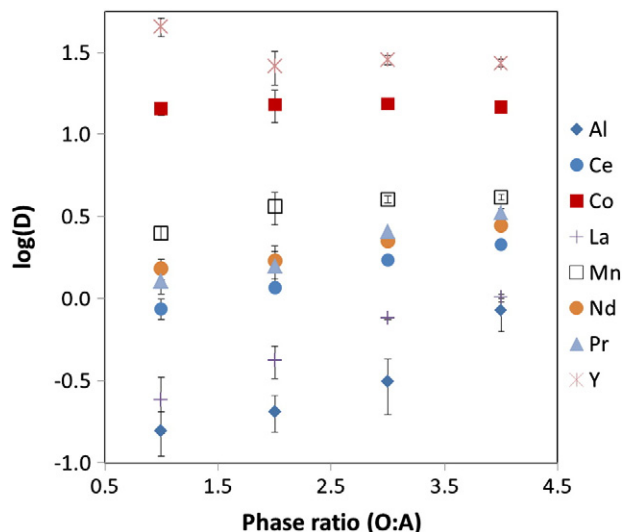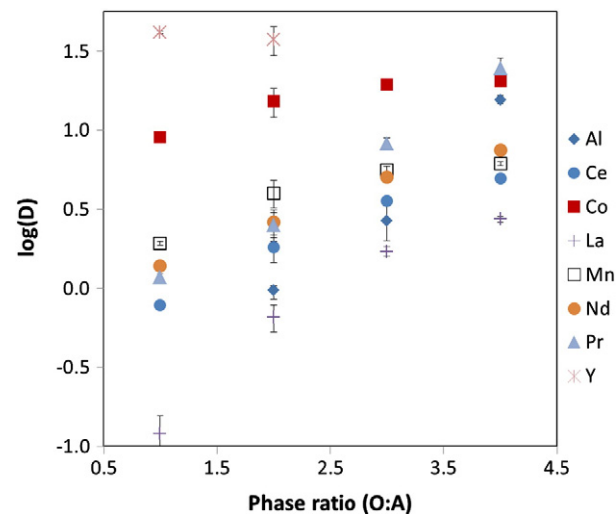

Fig. 3. Distribution ratios for 8 M chloride leach solutions based on mixed electrode material, see Table 1 for concentrations, with a 70% Cyanex 923, 10% TBP and 20% kerosene concentration. Zinc and iron excluded due to their high distribution ratios. Nickel, potassium and magnesium excluded due to their low distribution ratios.

Table 2
Distribution ratios when stripping an organic phase after extraction from a leach liquor based on cathode material with various stripping agents, O:A 1:1. Missing iron values were below detection limits in the aqueous phase.

	1 M NaNO$_3$	1 M HNO$_3$	5 M HNO$_3$	1 M NaCl	1 M HCl
Al	>100	0.08 ± 0.03	<0.1	0.55 ± 0.3	<0.1
Co	0.27 ± 0.1	<0.1	<0.1	0.14 ± 0.1	0.16 ± 0.1
Fe			13.3 ± 1		
Mn	3.5 ± 0.3	<0.1	<0.1	<0.1	<0.1
Ni	0.2 ± 0.1	<0.1	0.08 ± 0.1	0.09 ± 0.1	0.09 ± 0.1
Y	>100	26.8 ± 1.4	5 ± 0.4	0.27 ± 0.1	<0.1
Zn	>100	>100	0.18 ± 0.1	>100	>100

Table 3
Distribution ratios when stripping an organic phase after extraction from a leach liquor based on anode material with various stripping agents, O:A 1:1. Missing iron values were below detection limits in the aqueous phase.

	1 M NaNO$_3$	1 M HNO$_3$	5 M HNO$_3$	1 M NaCl	1 M HCl
Al	9.2 ± 2.3	<0.1	<0.1	1.6 ± 0.68	<0.1
Ce	>100	3.7 ± 0.01	0.75 ± 0.04	0.21 ± 0.02	<0.1
Co	0.33 ± 0.09	0.15 ± 0.04	0.19 ± 0.1	0.3 ± 0.03	0.3 ± 0.11
Fe			13 ± 7.9		
La	>100	0.87 ± 0.15	0.08 ± 0.12	<0.1	<0.1
Mn	0.49 ± 0.13	0.06 ± 0.13	0.07 ± 0.11	0.22 ± 0.03	0.18 ± 0.09
Nd	>100	6.8 ± 0.41	1 ± 0.05	0.28 ± 0.04	0.09 ± 0.04
Ni	0.18 ± 0.08	0.04 ± 0.07	0.09 ± 0.07	0.16 ± 0.07	0.1 ± 0.06
Pr	>100	4.8 ± 1	0.8 ± 0.18	0.2 ± 0.06	0.13 ± 0.11
Y	>100	13.5 ± 0.94	6 ± 0.74	1.1 ± 0.39	0.33 ± 0.12

co-extracted metals and be subsequently returned to the dissolution of new material together with concentrated hydrochloric acid to raise the chloride concentration to 8 M.

4.2. Extraction behavior of chloride based anode leach solutions with Cyanex 923

The distribution ratios for different phase ratios in the extraction system based on the anode leach solutions are shown in Fig. 2. The distribution ratio of lanthanoids is too low to be suitable in a process, especially for lanthanum, at lower phase ratios. Cobalt, manganese and yttrium are preferentially extracted and increasing the phase ratio does not sufficiently raise the extraction of lanthanoids.

The lanthanum and aluminium distribution ratios remain relatively low even at phase ratio 4:1. This is likely to be a loading effect coupled with a lowering of the chloride concentration leading to low lanthanum extraction even for high phase ratios. Assuming the trivalent and divalent metals to be extracted as uncharged chloride complexes the reduction in chloride concentration in the aqueous phase is 3.7 M (assuming constant volume). This is a large reduction and explains the low lanthanum distribution ratio.

The chloride influence was investigated at phase ratio 3:1 by adding solid potassium chloride (reagent grade, Scharlau) to raise the chloride content, when saturated with potassium chloride the increase in distribution ratio for lanthanum was from 0.8 to 1.6. This indicates that the reduction in chloride concentration after extraction in the tested systems has a significant influence on the distribution ratios.

Adding 8 M hydrochloric acid was also investigated as a means to retain the chloride level in the system by reducing metal concentration while maintaining chloride levels. This method was found to be unsuccessful since the increased acidity reduced the extraction of aluminium and rare earth metals. Two actions that increase the distribution ratios of the metals with too low values in a process are to use counter-current systems as this will raise the chloride content in the later steps and to reflux a part of the purified nickel flow in order to lower the amount of metals to be extracted.

4.2.1. Stripping characteristics

The ability to strip a loaded organic phase after contacts with a anode based leach liquor was investigated for chloride and nitrate solutions with and without acidity using sodium salts and acids, the results are presented in Table 3.

The stripping characteristics are similar to the cathode case with a possibility to retain the rare earth elements in the organic phase. In a nitrate system with low acidity (1 M NaNO$_{3(aq)}$) the rare earth elements and iron are not stripped and remain in the organic phase. Aluminium has a distribution ratio of 9.2 and will give some impurity if used for the stripping of cobalt and manganese. Increasing the acidity (1 and 5 M nitric acid) increases the stripping of the rare earth elements. With a chloride stripping agent all elements except iron (if present) can be stripped. Increased acidity decreases the distribution ratios in the chloride systems. Similar to the cathode case the

loaded organic phase contained less than 1% of the nickel and potassium in the original aqueous phase.

4.2.2. Reflux

A reflux with the purpose of raising the nickel content in the feed was simulated using a 4 M nickel chloride solution. The distribution ratios from the reflux test at 50%, the necessary level for lanthanum to reach a sufficiently high a distribution ratio, are shown in Table 4. At this reflux level the loading capacity is sufficiently high and the chloride concentration remains sufficiently high to allow extraction. This limit on the reflux level can be considered the upper value; the actual required reflux level can be lower since the chloride profile in a counter-current set-up will influence the distribution ratio favorably compared to the batch test.

4.3. Extraction behavior of chloride based mixed material leach solutions with Cyanex 923

For the 8 M chloride mixed material system, shown in Fig. 3, zinc was quantitatively extracted and the extraction of lanthanoids was low for low phase ratios. The extraction of nickel, potassium and magnesium remains below detection limits for higher phase ratios of 3 and 4 where the distribution ratios are higher for the lanthanoids. Cobalt and yttrium are preferentially extracted and has a distribution ratio for the tested phase ratios.

Similarly to the anode case, the chloride influence was investigated at phase ratio 3:1 by adding potassium chloride to raise the chloride content, when saturated the increase in distribution ratio for lanthanum was from 1.7 to 3.8. This indicates that the reduction in chloride concentration after extraction in the tested systems has a significant influence on the distribution ratios.

4.3.1. Stripping characteristics

The ability to strip a loaded organic phase after contacts with a leach liquor based on mixed material was investigated for chloride and nitrate solutions with and without acidity using sodium salts and acids, the results are presented in Table 5. The distribution ratios are similar to the anode material case with a possibility to retain the trivalent elements and zinc in the organic phase by stripping with sodium nitrate. This only strips the cobalt, manganese and any present nickel impurity. Aluminium has a distribution ratio of 9.7 and

Table 4
Distribution ratios for 50% reflux in the extraction from the liquor based on anode material at O:A ratio 2:1.

Al	Ce	Co	Fe	La
56 ± 3.4	15 ± 0.45	90 ± 2.3	>100	6 ± 0.13
Mn	Nd	Pr		Y
20 ± 0.7	22 ± 1.4	20 ± 0.6		>100

Table 5
Distribution ratios when stripping an organic phase after extraction from a leach liquor based on mixed material with various stripping agents, O:A 1:1. Missing iron values were below detection limits in the aqueous phase.

	1 M NaNO$_3$	1 M HNO$_3$	5 M HNO$_3$	1 M NaCl	1 M HCl
Al	37.7 ± 3.1	0.15 ± 0.18	0.14 ± 0.06	3.5 ± 2	0.13 ± 0.07
Ce	>100	4.5 ± 0.78	0.92 ± 0.05	0.23 ± 0.06	<0.1
Co	0.16 ± 0.05	0.03 ± 0.08	<0.1	0.18 ± 0.1	0.07 ± 0.04
Fe	>100		9.7 ± 2.3		
La	>100	1.7 ± 0.11	0.39 ± 0.08	0.38 ± 0.13	0.2 ± 0.06
Mn	0.9 ± 0.11	0.13 ± 0.09	0.07 ± 0.06	0.28 ± 0.14	0.06 ± 0.07
Nd	>100	7.5 ± 0.79	1 ± 0.09	0.18 ± 0.1	<0.1
Ni	0.15 ± 0.07	<0.1	<0.1	0.2 ± 0.11	<0.1
Pr	>100	5.8 ± 1.3	0.88 ± 0.19	0.24 ± 0.15	0.05 ± 0.08
Y	>100	13.7 ± 1.5	5.3 ± 0.46	1 ± 0.38	0.04 ± 0.08
Zn	>100	>100	1.2 ± 0.11	>100	>100

Table 6
Distribution ratios for 40% reflux in the extraction from the liquor based on mixed material at O:A ratio 2:1.

Al	Ce	Co	Fe	La	Mg
25 ± 24	24 ± 0.6	71 ± 3.8	>100	11 ± 0.28	0.04 ± 0.001

Mn	Nd	Ni	Pr	Y	Zn
17 ± 0.7	34 ± 0.7	0.015 ± 0.004	65 ± 2.4	>100	>100

will give some impurity if used for the stripping of cobalt and manganese. Increasing the acidity (1 and 5 M nitric acid) increases the stripping of the rare earth elements. With a chloride stripping agent all elements but iron (if present) can be stripped. Increased acidity decreases the distribution ratios in the chloride systems. The zinc has a high distribution ratio except in the 5 M nitric acid. This is likely to be due in part to the amount of chloride ions released when the chloride complexes are stripped from the organic phase. As for the cathode and anode cases the loaded organic phase contained less than 1% of the nickel and potassium in the original aqueous phase.

4.3.2. Reflux

Similarly to the anode case the reflux level for the mixed system was simulated using a 4 M nickel chloride solution and a O:A ratio of 2:1. The distribution ratios from the reflux test at 40% v/v reflux is shown in Table 6. As described for the anode case this is a upper limit value.

4.4. Discussion

The distribution ratios of the metals are higher in the case based on dissolved cathode material and lowest for the dissolved anode material. This can be explained by the lowered chloride concentration due to the loss of chloride ions in the aqueous phase since the extracted metal complexes are neutral by the inclusion of chloride ions. Accordingly the reduction in concentration is equivalent to the extracted metal concentration multiplied with the metal oxidation state. The amount of non-nickel metals is highest in the anode material and lower in the cathode material; this explains why the chloride influence on the distribution ratio is greater for the extraction of dissolved anode material.

The loading and chloride-loss influence on the extraction systems for the anode and mixed material systems can be counteracted by refluxing part of the nickel-rich raffinate after extraction to the dissolution step. Concentrated hydrochloric acid would be added to the reflux, raising the chloride content back to 8M (extraction would have lowered it), which would then be used for dissolution of more solid material. This would increase the concentration of nickel in the feed and decrease the amount of metals to be extracted and reduce loading and chloride loss for the extraction system.

However, using counter-current processes reduces the need for reflux for the extraction step, as a greater chloride extraction can be allowed for than can be shown in batch experiments, since the chloride concentration profile is such that the final step has the highest chloride concentration. This means that the systems need to be tested under more process-like conditions and this is underway.
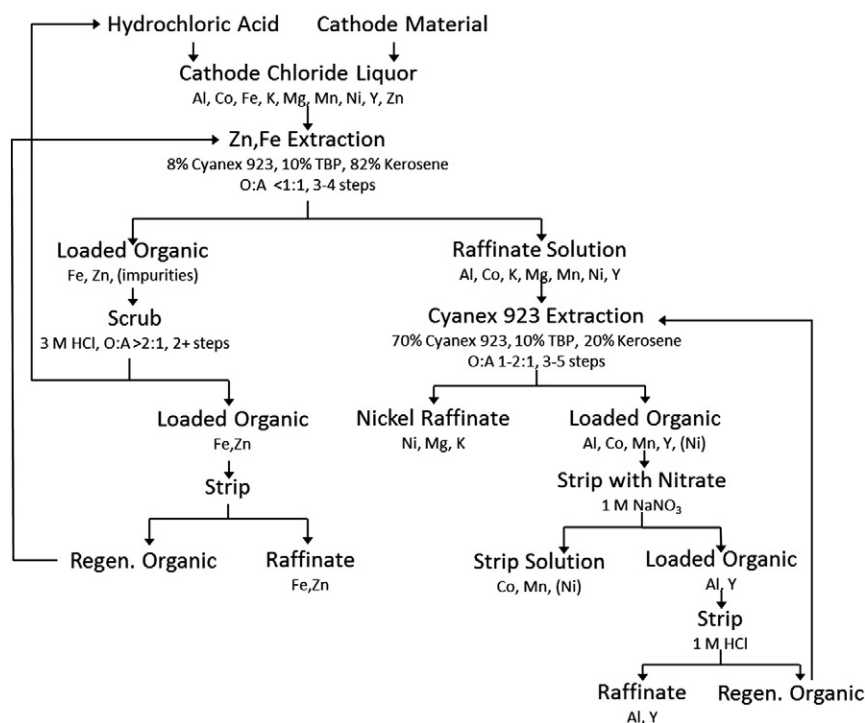
Fig. 4. A potential process for a system based on cathode leach liquors. The number of steps is calculated based on ideal systems requiring more than 99% purity.
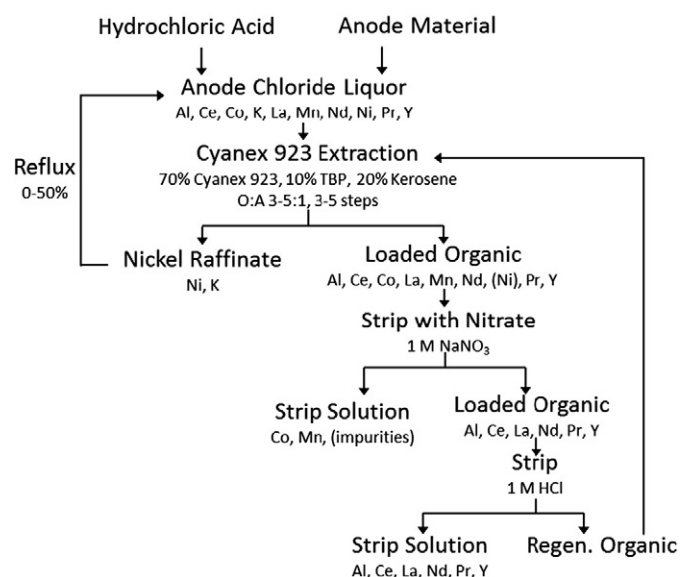
Fig. 5. A potential process for a system based on anode leach liquors. The number of steps is calculated based on ideal systems requiring more than 99% purity.

4.5. Separation processes

The results of the presented experiments indicate that a counter-current process can be created using Cyanex 923. Some possible process systems are suggested for the individual electrode materials and the combined mixed material.

An extraction scheme based on dissolved cathode material is shown in Fig. 4 separating the 7 main cathode metals and aluminium and iron into four fractions. The first step in the scheme is to remove zinc and iron from the feed by using a diluted Cyanex 923 organic phase, since it can be difficult to strip from the high extractant concentration organic phase. The extract from the pre-step can then be scrubbed using an acidic chloride solution. However, with a

suitable strip for zinc from the main extraction the pre-step is not strictly necessary. All metals other than nickel, potassium and magnesium are extracted in the main step using a 70% Cyanex 923 organic phase. The organic phase loaded with aluminium, cobalt, manganese and yttrium (potentially some nickel impurity) can be stripped directly with a low concentration chloride solution or a separation of the aluminium and yttrium can be achieved by using a nitrate strip solution.

An anode extraction scheme is shown in Fig. 5. Direct application of the 70% Cyanex 923 organic solvent on the original leach liquor removes a large amount of the chloride content and loads the solvent, thereby making the lanthanoid extraction difficult. This can be counteracted by refluxing a part of the nickel raffinate flow, thereby lowering the amount of metals to be extracted. Hydrochloric acid is added to the refluxed flow and used for dissolution which will take the chloride concentration back to 8 M. The nickel, which is not extracted, will be a more significant part of the flow and less of the minor metals need to be extracted in the main step, thereby reducing loading. Note that iron is not included in the extraction scheme, since the pure anode material has no iron. Iron is present if it is contaminated by the electrode support material. The organic phase loaded with aluminium, cobalt, manganese, lanthanoids, yttrium and a nickel impurity can be stripped directly with a low concentration chloride solution or a separation of the aluminium, lanthanoids and yttrium can be achieved by using a nitrate strip solution. The latter case is used in Fig. 5 and the remaining extracted metals can thereafter be stripped using an acidic chloride solution.

The mixed material extraction scheme is shown in Fig. 6 and has both the characteristics of the anode and cathode cases since the zinc and iron content is to be extracted in a pre-step using a diluted Cyanex 923 organic phase, and part of the nickel raffinate needs to be refluxed to reduce loading and raise the chloride concentration after extraction. The needed reflux level is slightly lower since the nickel content is higher than for the anode based system.

Further separations of the final raffinate fractions, such as the cobalt from manganese or magnesium and potassium from nickel or other mixtures can be separated more efficiently using reagents other than Cyanex 923.
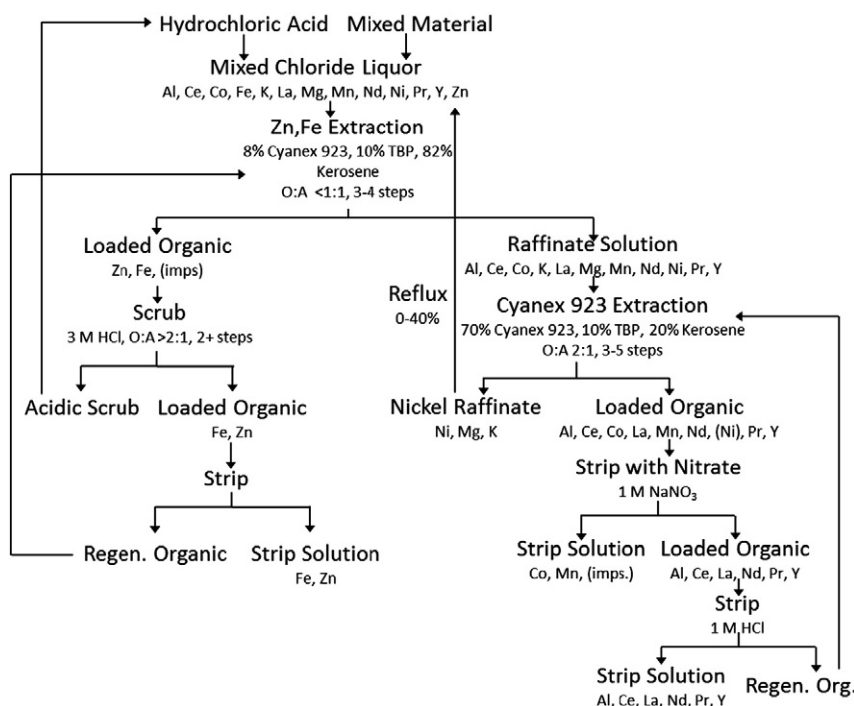

Fig. 6. A potential process for the solution based on a mixed material. The number of steps is calculated based on ideal systems requiring more than 99% purity.

5. Conclusions

Three separation process schemes for 8 M hydrochloric acid leach solutions from nickel metal hydride batteries using the solvating extractant trialkylphosphine oxide mixture Cyanex 923 have been developed. The batteries used in the study contained thirteen metals and were separated in up to four fractions based on chemical properties, thereby reducing the complexity of individual separations. Suitable initial conditions were found to selectively extract all elements excluding nickel, potassium and magnesium.

As for any solvent extraction system the efficiency of this process depends on the input phase. However, in this particular process changes in concentration can be compensated for by changing the reflux level or the phase ratio. Unless the system is optimized it is likely that a small part of the nickel will be extracted in all three systems and be part of the cobalt and manganese stream after stripping. This could be solved with a nickel scrub step or a purification with regard to nickel could be achieved during a separation of cobalt and manganese.

Acknowledgements

References

Dessouky, S.E., El-Nadi, Y., Ahmed, I., Saad, E., Daoud, J., 2008. Solvent extraction separation of Zn(II), Fe(II), Fe(III) and Cd(II) using tributylphosphate and Cyanex 921 in kerosene from chloride medium. Chem. Eng. Process. 47, 177–183.

Dziwinski, E., Szymanowski, J., 1998. Composition of Cyanex 923, Cyanex 925, Cyanex 921 and TOPO. Solvent Extr. Ion Exch. 16, 1515–1525.

Flett, D.S., 2005. Solvent extraction in hydrometallurgy: the role of organophosphorus extractants. J. Organomet. Chem. 690, 2426–2438.

Gupta, B., Tandon, S.N., Deep, A., 2002. Recovery of cobalt and nickel from spent catalysts using Cyanex 923. Proceedings of the International Solvent Extraction Conference, ISEC 2002, pp. 793–797.

Gupta, B., Deep, A., Singh, V., Tandon, S., 2003. Recovery of cobalt, nickel, and copper from sea nodules by their extraction with alkylphosphines. Hydrometallurgy 70, 121–129.

Haynes, W.M. (Ed.), 2011. CRC Handbook of Chemistry and Physics 2011–2012, 92nd edition.

Ito, M., Kashiwaya, K., Sumiya, N., Hiroyoshi, N., Tsunekawa, M., 2009. Anode activating agent recovery by magnetic separation from the <0.075 mm fraction of crushed nickel metal hydride batteries from hybrid vehicles. Sep. Purif. Technol. 69, 149–152.

Larsson, K., Ekberg, C., Ødegaard-Jensen, A., in press. Dissolution and characterization of HEV NiMH batteries. Waste Manag. http://dx.doi.org/10.1016/j.wasman.2012.06.001.

Li, L., Xu, S., Ju, Z., Wu, F., 2009. Recovery of Ni, Co and rare earths from spent Ni-metal hydride batteries and preparation of spherical Ni(OH)$_2$. Hydrometallurgy 100, 41–46.

Reddy, B.R., Priya, D.N., 2006. Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel-cadmium, batteries using cyanex 923 and 272. J. Power Sources 161, 1428–1434.

Reddy, M., Varma, R., Ramamohan, T., 1998. Cyanex 923 as an extractant for trivalent lanthanides and yttrium. Solvent Extr. Ion Exch. 16, 795–812.

Rodrigues, L.E.O.C., Mansur, M.B., 2010. Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel-metal-hydride batteries. J. Power Sources 195, 3735–3741.

Saji, J., Rao, T., Iyer, C., Reddy, M., 1998. Extraction of iron(III) from acidic chloride solutions by Cyanex 923. Hydrometallurgy 49, 289–296.

Tsunekawa, M., Ito, M., Furuya, H., Hiroyoshi, N., 2007. The recovery of electrode compounds from waste nickel metal hydride batteries by physical separation techniques. Mater. Trans. 48, 1089–1094.

Tzanetakis, N., Scott, K., 2004. Recycling of nickel-metal hydride batteries. I: dissolution and solvent extraction of metals. J. Chem. Technol. Biotechnol. 79, 919–926.

Zhang, P., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1998. Hydrometallurgical process for recovery of metal values from spent nickel-metal hydride secondary batteries. Hydrometallurgy 50, 61–75.

Zhang, P., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1999. Recovery of metal values from spent nickel-metal hydride rechargeable batteries. J. Power Sources 77, 116–122.